Division of Engineering
BROWN UNIVERSITY
PROVIDENCE, R. I.

A QUASICHEMICAL APPROACH
TO ADSORPTION AND THE
RECOMBINATION OF SURFACE BONDS

M. H. RICHMAN and R. D. FRENCH

American Iron and Steel Institute
Contract Grant 200

Advanced Research Projects Agency
Department of Defense
Contract SD-86
Materials Research Program

AISI 200/1
ARPA E60

October 1968

A Quasichemical Approach to Adsorption

and the Recombination of Surface Bonds*

by

Marc H. Richman[†] and Robert D. French[††]

[†]Div. of Engineering, Brown University, Providence, R. I.

[††]U.S. Army Materials and Mechanics Research Center, Watertown, Mass.

Abstract

A quasi-chemical model is presented and applied to the adsorption of tungsten on specific crystallographic planes of tungsten. The use of this method requires the assumption of a certain degree of recombination of electron orbitals from surface and subsurface atoms. A set of rules for recombination of bonding is presented and the results calculated using this method are in good agreement both with experimentally determined values of desorption enthalpies and with the tabulated enthalpy of sublimation for tungsten.

Introduction

The adsorption of atoms and molecules onto clean metal surfaces and the subsequent desorption of these atoms or molecules has been studied by a variety of methods such as low energy electron diffraction, field emission microscopy and field ion microscopy. While considerable progress has been made in understanding the adsorption and desorption of gas atoms and molecules in association with metal surfaces, there are still serious questions to be answered. Perhaps the problem most pertinent to field ion microscopists is to explain the phenomenon of hydrogen promotion of ion images reported by Müller (1) and attributed by him to the formation of new orbitals involving electrons from both the hydrogen and the metal atoms. Another serious question concerns the bonding at the surface of a metallic crystal and the extent of bond recombination, suggested by Richman (2), that occurs at the surface. Furthermore, the problem of metal atoms adsorbed onto their own lattice (i.e. self adatoms) requires further examination and the computation of interatomic forces and binding energies. This particular problem has been studied by both Ehrlich and Kirk (3) and Plummer and Rhodin (4).

This paper is an attempt to provide a simplified quasi-chemical explanation - admittedly only an approximation - to the recombination of surface bonds and the adsorption and desorption of metal adatoms on their own lattice. While a more rigorous treatment is necessary, the present method does offer an explanation of the experimental observations and allows further extrapolations to be made.

Procedure

An adsorbed atom occupies a low energy site on a particular crystallo-graphic surface of a metal. From a hard-sphere model, it could be said that an adatom lies in a depression in the surface. For example, let us consider the (100) surface of a body-centered cubic metal. The hard sphere model (after Nicholas (5)) is shown in Fig. 1. Any adatom on this surface should occupy a position touching the four atoms forming the basic square cell (i.e. the basic (100) unit cell) of this surface. In this case, then, the adatom occupies a position which is simply a normal lattice position, i.e. its coordinates could be found by a simple translation vector from the position of an atom in the surface or below it. This may be more evident in Fig. 2 where the positions of the surface atoms and the adatom are given schematically. The adatom here is in direct contact with the four atoms forming the corners of the (100) face and is displaced from the body-centered position (just below the surface) by the vector [100] a.

There are cases, however, where the adsorbed atom does not rest in a normal lattice site (as explained above), but in a site whose occupancy represents a state of lower energy than that of a normal lattice site. In this case the coordination between the adatom and the i-th nearest neighbors will differ from the same coordination in the bulk material - a fact that must be borne in mind when calculating energies of desorption.

When a fresh (clean) surface is created by cleavage or a suitable surface is produced by field evaporation, the surface atoms may be assumed to occupy the positions on the normal three-dimensional lattice. This assumption is based on the fact that field ion microscopy has provided better evidence of a change in surface structure. There is, however, little reason

to expect that the bonds cut by the surface plane maintain their original,
bulk, geometrical positions. The bonds are not rigid connections as we are
accustomed to use in our model-building, but are electron orbitals whose
shape and orientation are dependent on the solutions of the wave equations.
An orbital cut by the surface may retain its original shape and orientation
or undergo a recombination, i.e. pair off with an electron orbital from
another surface atom to achieve a lower energy state for the system.

Once the surface atoms have undergone recombination, an adatom will
only be able to reestablish certain bonds with these surface atoms. To
illustrate this point, let us consider the arrangement of four surface atoms
and one subsurface atom shown in Fig. 3a. Prior to recombination, or if one
does not consider it, there are five bonds leading to the adatom position.
Four of these bonds originate from surface atoms (the solid lines) and one
from the subsurface atom (the broken line). Recombination occurs where
there is an orbital overlap established between these various atoms comprising
the surface. The ultimate or most complete recombination would be that shown
in Fig. 3b where the four solid bonds to the adatom position (of Fig. 3a)
are now spread about among the four surface atoms and the (broken-line) bond
from the subsurface atom has changed to bonds to all four surface atoms. In
this way there would be no broken bonds and the surface would have a higher
energy than the bulk due to the different orbital arrangement and electron
density pattern.

If recombination does occur but not to its most complete extent, the
probability would be that subsurface bonds would be recombined whereas surface
ones would not. Thus an adatom sitting on the surface depicted in Fig. 3
would bond to only the surface atoms and not to any of the subsurface ones.

An example would be that of the (100) body-centered cubic surface. The adatom here would have four first nearest neighbors at a distance of a $\sqrt{3}/2$ (i.e. direct contact) as in the normal case, but the second-nearest neighbors which correspond to the atom a distance a immediately below the adatom position would have undergone recombination and therefore no second neighbor bond would be established here. Similarly second-nearest neighbors in the plane of the surface would have also recombined. A similar geometrical feature has been suggested by Plummer and Rhodin to explain some of their results.

To utilize, therefore, the concept of recombination of surface bonds, in studying adsorption, certain guidelines may be established. They are as follows:

1. Subsurface atoms will always recombine to form new orbitals with surface atoms.

2. For any adatom, direct contact means the establishment of a normal nearest-neighbor bond. This holds whether the adatom is in contact only with surface atoms or with subsurface atoms as well.

3. Bonds from surface atoms to adatoms are subject to screening and geometrical tendencies to be recombined. Thus bonds at distances greater than 2nd neighbors are usually not contributive to the desorption energy.

Using these three rules as guides, the numbers of first and second-nearest neighbors can be calculated for an adatom on various crystallographic faces of a body-centered cubic crystal.

In the case of the (100) surface (Fig. 2) there are four nearest neighbors at 0, A,B, and C and no second nearest neighbors. The adatom position also is shown directly above .1 . An adatom on the (110) surface (Fig. 4) has three first neighbors at 0,B, and C and 1 second nearest neighbor

in the [1$\bar{1}$0] direction. For the (111) surface, two possible adatom sites

exist. The lowest energy (and therefore most stable) site is shown in Fig. 5

where the adatom (directly above .2 and in contact with it has nearest

neighbor bonds with 0,A,C, and .2 and 3 second neighbor bonds with atoms of

the type 0.1. Another possible site would have the adatom touching B,C, and

0.1. The adatom positions for the (112), (103), (123), and (114) surfaces are

shown in Figs. 6-9.

The results of this study are summarized in Table I. There are two

choices of adatom sites for the (111), (103), (123), and (114) planes. The

higher energy site is indicated by square brackets [].

In order to see if this quasichemical approach can explain measured

desorption energies, one must know the manner in which the interatomic forces

decay with distance. If we consider metals, e.g. the adsorption of tungsten

on tungsten, the interatomic forces are short range and a sixth power decay,

may be used to represent the force between i-th nearest neighbors, i.e.

$$F_i = k_i/d_i^6 \tag{1}$$

where k_i is a constant and d_i the interatomic distance. Now the energies

of the various bonds can be calculated using the relation

$$E_i = \frac{dF_i}{dd_i} \tag{2}$$

and the assumption that the energies of such bonds are additive.

Results and Discussion

Taking the experimental values of the enthalpy of desorption as

measured by Ehrlich and Kirk and Plummer and Rhodin for each surface, the

first nearest neighbor bond energy E_1 can be found by dividing the desorption

TABLE I

Calculated Bond Energies*

(hkℓ)	n_1	d_1/a	n_2	d_2/a	ΔH (expt'l)	E_1 (calc)
100	4	$\sqrt{3}/2$	-	-	8.0	2.0
110	3	$\sqrt{3}/2$	1	$\sqrt{5}/2$	5.9	1.7
111	4	$\sqrt{3}/2$	3	1	6.7	1.2
	[3	$\sqrt{3}/2$	1	1	6.7	1.9]
112	3	$\sqrt{3}/2$	2	1	6.9	1.7
103	4	$\sqrt{3}/2$	1	1	6.6	1.5
	[3	$\sqrt{3}/2$	1	1.1	6.6	2.0]
123	3	$\sqrt{3}/2$	2	1	6.6	1.7
	[3	$\sqrt{3}/2$	1	1	6.6	1.9
114	4	$\sqrt{3}/2$	2	1	6.2	1.2
	[3	$\sqrt{3}/2$	1	$\sqrt{2}$	6.2	2.0]

* Based on inverse 6th power force decay

enthalpy by the total adatom bond energy (in terms of E_1). These values are listed in Table I. The values of E_1 are averaged for those cases where two possible sites for adsorption exist and the results are shown in Table II. The relative constancy in the value of E_1 is evidence of agreement between the quasi-chemical approach and experiment.

A further note of agreement is found in the two values of desorption enthalpy noted by Ehrlich and Kirk for the (321) plane of tungsten. They reported that some adatoms, even at the center of the plane, are removed at a voltage 20% below that required for other atoms (i.e. for clearing the plane), and they suggest the possibility of two different state of bonding. This difference is to be distinguished between that found by Ehrlich and Kirk and Plummer and Rhodin for atoms at the center versus the edge of any given plane. For the (321) plane, the present calculations (see Table I) indicate a difference in total bond energy of 14% in reasonable agreement with experiment. This would indicate that the adatoms desorbed at the 20% lower voltages were bonded in the higher energy sites with 3 first and 1 2nd nearest neighbor bonds whereas the adatoms desorbed at 6.6eV were in the lower energy sites having 3 first and 2nd neighbor bonds. Ehrlich and Kirk also mention occasional observations of similar effects on other planes except the (110). Table I predicts that both the (100) and (110) should not be subject to the dual bonding.

The heat of sublimation of a substance is the enthalpy required to convert one made of the materials from the crystalline form to individual unbonded atoms at a particular temperature. Using the average value of $E_1 = 1.74$ eV as the enthalpy of a first nearest neighbor bond at 78°K, the sublimation enthalpy (due to interatomic bonding)

TABLE II

Average Bond Energies*

(hkℓ)	E_1(ev)
100	2.0
110	1.7
111	1.6
112	1.7
103	1.8
123	1.8
114	1.6

* Based on inverse 6th power force decay.

$$\Delta H = \frac{1}{2} N_o \sum_i Z_i E_i \qquad (3)$$

where Z_i is the i-th coordination number and N_o is Avagodro's number. Using equations (1) and (3) and considering only first and second nearest neighbors, the sublimation enthalpy of tungsten at 78°K is 219 kcal/mole. The experimental value as listed in the literature is 229 kcal/mole for this same temperature; in good agreement with the quasi-chemical approximation.

The 4.5% discrepancy between calculated and experimental values can be attributed to several sources of error. (1) the cut-off of equation (3) at 2nd-nearest neighbors - using 3rd or 4th nearest would give a higher value and (2) an underestimate of the extent of recombination - if more bonds were recombined the computed value of E_1 would be greater and so would the value of sublimation enthalpy.

The agreement between the calculations based on this quasi-chemical approximation and independent experimental evidence would indicate that such an approach to adsorption, desorption, and the recombination of surface orbitals can be of assistance in interpreting results of pulsed-desorption experiments and other surface sutides. The method is not intended to fully explain the nature of the interatomic forces or orbital overlap and super-exchange, but it should serve as an easily used tool in many investigations.

Conclusions

A quasi-chemical method has been presented to aid in the quantitative analysis of adsorption and desorption experiments. The model is an approximate one and is based on a set of rules for the recombination of electronic orbitals of surface and near surface atoms. This method is applied to the

case of adsorption of tungsten or tungsten with good agreement between
theory and experiment.

References

1. E. W. Müller, Z. f. Phys. Chem., 1967, 53, 1.

2. M. H. Richman, "Field Ion Microscopy in Physical Metallurgy and
    Corrosion", R. Hochman, B. Ralph, and E. W. Müller, Eds.,
    Georgia Institute of Technology Press, to appear   November 1968.

3. G. Ehrlich and C. F. Kirk, J. Chem. Phys., 1968, 48, 1465.

4. E. W. Plummer and T. N. Rhodin, XIV Fluid Emission Symposium, Washington,
    D. C., June, 1967.

5. J. F. Nicholas, "Atlas of Models of Crystal Surfaces", Gordon & Breach,
    New York, 1965.
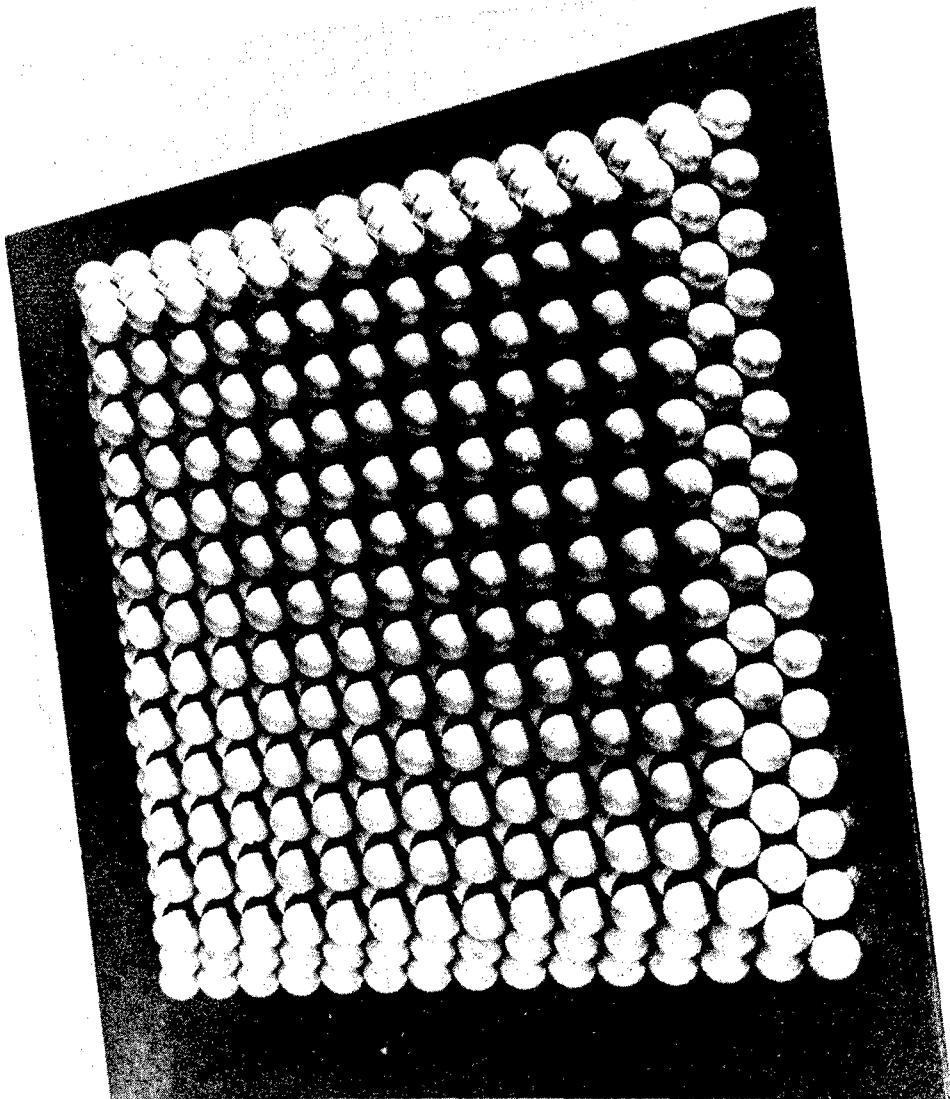
Fig. 1 Hard-Sphere Model of (100)-B.C.C. Surface
after Nicholas(5).
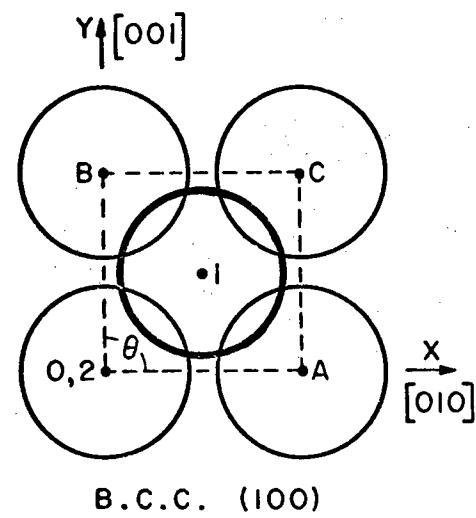
Fig. 2   Adatom Position on the (100)-B.C.C. Surface.

(a)   (b)

NO RECOMBINATION   AFTER RECOMBINATION
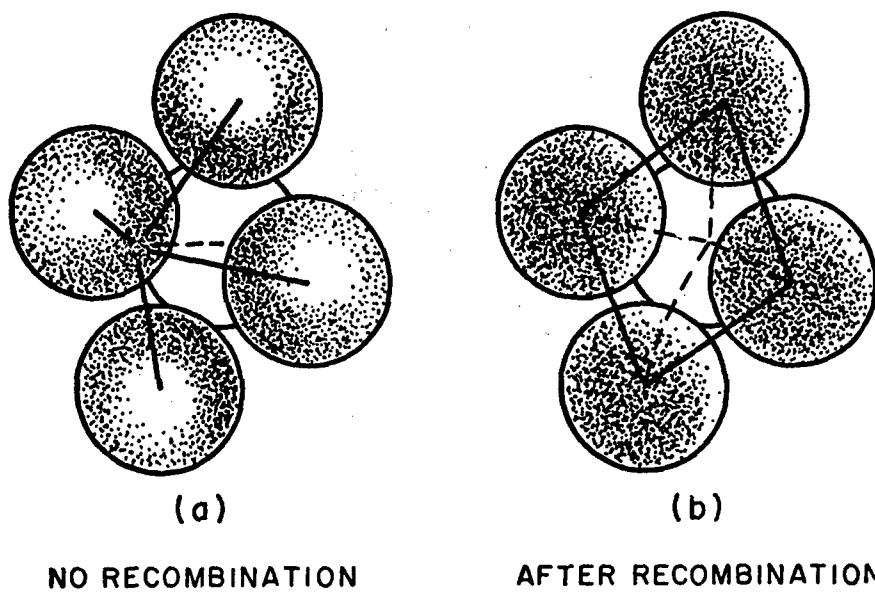

Fig. 3   Bonds at a Crystal Surface.
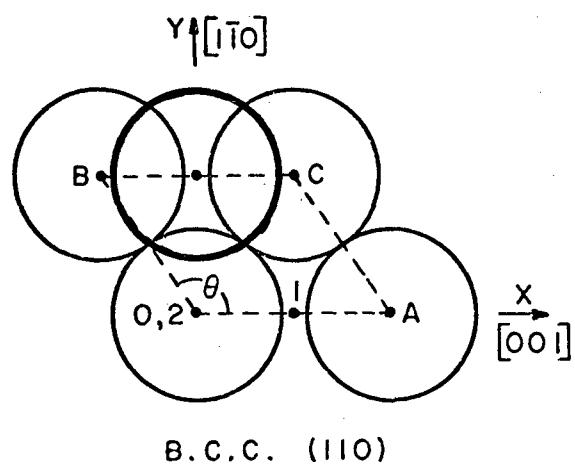
Fig. 4 Adatom Position on the (110)-B.C.C. Surface.
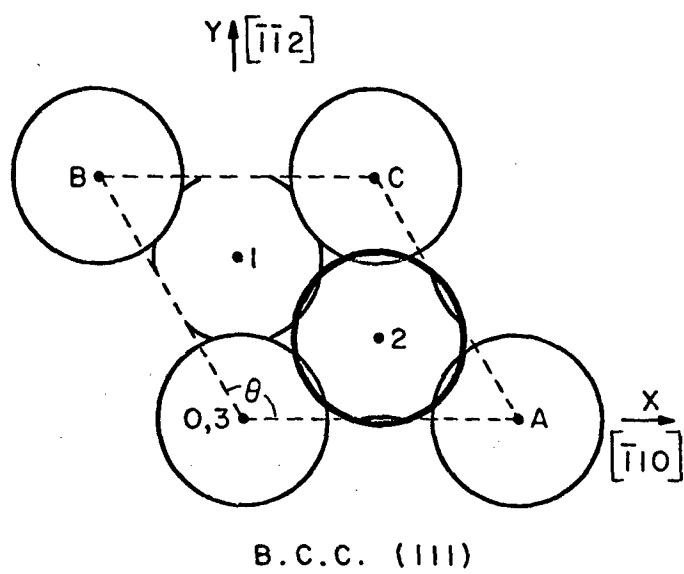
Fig. 5   Adatom Position on the (111)-B.C.C. Surface.
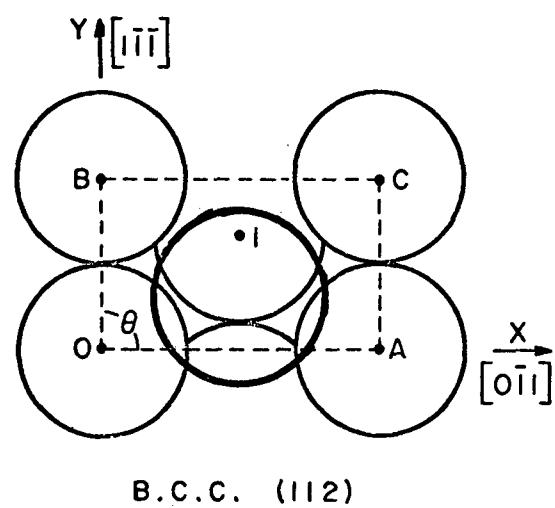
Fig. 6   Adatom Position on the (112)-B.C.C. Surface.
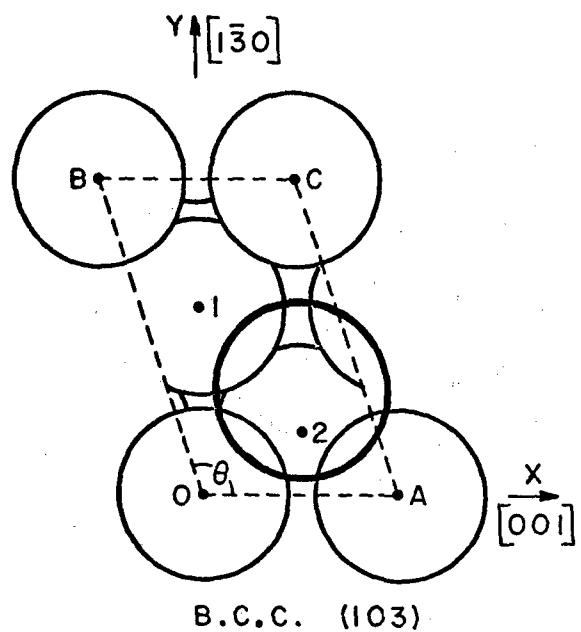
Fig. 7 Adatom Position on the (103)-B.C.C. Surface.
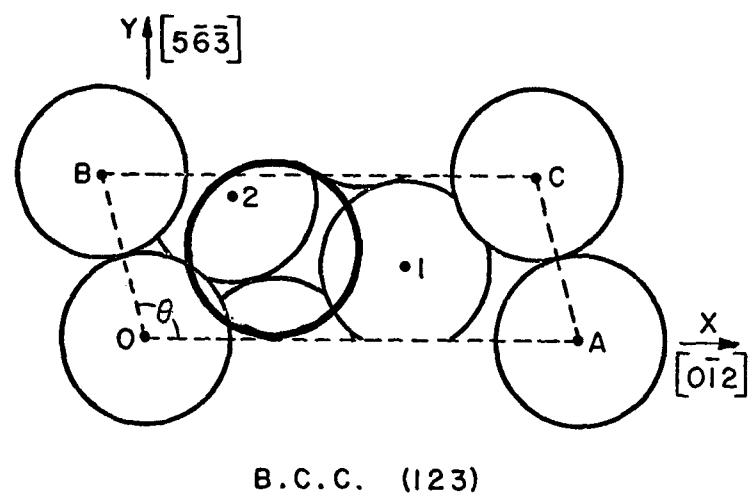
Fig. 8 Adatom Position on the (123)-B.C.C. Surface.
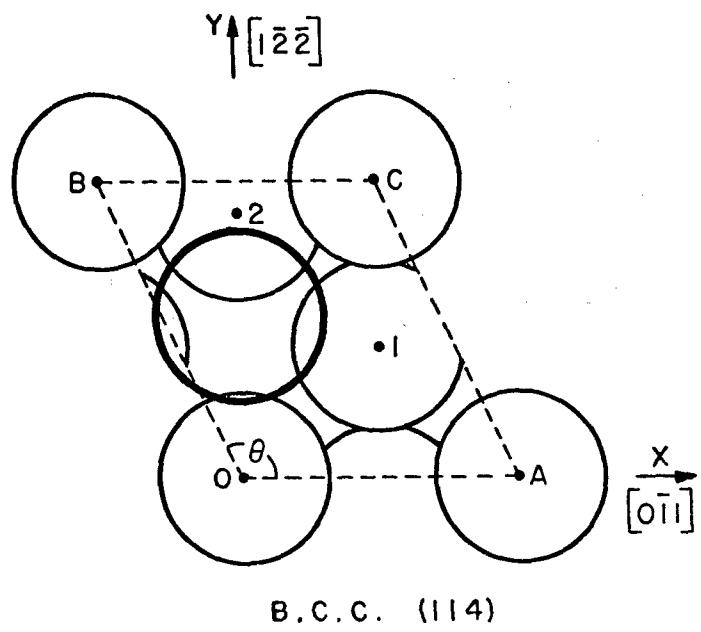
Fig. 9   Adatom Position on the (114)-B.C.C. Surface.